Studies on Corrosion of Metals by Viscoplastic Substances. IV.

On the Inhibitive Effect of Phosphate Compounds on the Corrosion of Metals by Viscoplastic Substances

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(1) Studies were made concerning the corrosion of aluminum in a viscoplastic medium prepared from calcium carbonate, and the inhibitive action of several phosphates. The results obtained showed that among several orthophosphates the alkali earth metal monobasic- and dibasic ones possess inhibitive action while among condensed phosphates sodium hexametaphosphate shows the same effect.

(2) The viscoplastic substance was stuffed into a metal tube and the authors measured the time needed for the expansion of the tube caused by the gas formation accompanying corrosion of the tube. The above mentioned time was converted to its logarithmic value and was named "the index of inhibition time". The results obtained by measuring the index of inhibition time, were similar to those of the measurement of corrosion potential. The measurement of the index of inhibition time proved to be an effective and significant means in the deduction of the corrosion behavior of viscoplastic substances.

(3) Aluminum powder was mixed into the viscoplastic substance and the corrosion behavior was measured by the X-ray diffraction method, which yielded the metallic aluminum left in the sample. The results obtained were similar to those of the corrosion potential and the index of inhibition time. The measurement of X-ray diffraction of metallic powder in a viscoplastic substance was very simple and provides significant means for the study of the corrosion in viscoplastic substances.

(4) Research carried out on the relationship between the concentration of magnesium hydrogen orthophosphate and the corrosion potential. The results obtained showed that the addition of an amount of magnesium hydrogen orthophosphate of 0.4 wt % (0.16% P_2O_5) was satisfactory for the inhibition of corrosion of aluminum.

(5) The addition of 0.2 wt % (0.13% P_2O_5) of sodium hexametaphosphate proved satisfactory for the inhibition of the corrosion of aluminum.

(6) Sodium hexametaphosphate was converted from the amorphous state to the crystalline sodium metaphosphate by thermal treatment, and the corrosion potential of the crystalline sample was tested. It was found to be toward a less noble value.

(7) In order to possess inhibitive properties, orthophosphates should slightly dissolve and react with metal. They should not release much free alkali, and the pH of viscoplastic substance should not be largely shifted towards the basic side.

1. Introduction

The corrosion of aluminum in a viscoplastic substance prepared from calcium carbonate, has been studied, using electrochemical methods. In a previous paper¹⁾, the authors reported the results of studies on the inhibitive effect and the mechanism of inhibition by silicate compounds against alkaline corrosive media.

In this paper, the following studies on the inhibition of corrosion of aluminum in viscoplastic substance by phosphate compounds, are described.

1) The study of corrosion under slightly

corrosive conditions can be greatly enhanced, by using the metal as a very fine power of very large surface area. The powder of the metal stays dispersed, and does not precipitate in substances as highly viscoplastic as those used in this research. Thus aluminum powder was mixed into a viscoplastic substance and its corrosive behavior was measured by the X-ray diffraction method.

2) When a viscoplastic substance reacts inside a closed container made of metal tube, the tube is expected to expand due to gas formation. The time needed for a certain degree of expansion of the tube

Table 1 pH and P₂O₅ (%) of Phosphate Specimens

	Oxide ratio	Classification	Phosphate		pH(1%) P ₂ O ₅ (%)		Structure
Condensed structure	1	Metaphosphate	Sodium hexameta phosphate	Na (H)	6.1	64.98	Ring Chain Two phosphorus atom
	1-2	Polyphosphate	Sodium tripolyphosphate	Na (T)	9.5	57.86	
	2	Pyrophosphate	Sodium pyrophosphate	Na (P)	10.3	31.84	
Simple structure	3	Orthophosphate	Trisodium orthophosphate (Tribasic sodium phosphate)	Na (3)	12.0	18.58	One phosphorus atom
			Disodium hydrogen orthophosphate (Dibasic sodium phosphate)	Na (2)	9.3	19.72	
			Sodium dihydrogen orthophosphate (Monobasic sodium phosphate)	Na (1)	5.1	51.07	
			Tricalcium diorthophosphate (Tribasic calcium phosphate)	Ca (3)	12.3	44.36	
			Calcium hydrogen orthophosphate (Dibasic calcium phosphate)	Ca (2)	8.3	41.38	
			Calcium tetrahydrogen diorthophosphate (Monobasic calcium phosphate)	Ca (1)	3.7	57.01	
			Trimagnesium diorthophosphate (Tribasic magnesium phosphate)	Mg (3)	9.6	34.18	
			Magnesium hydrogen orthophosphate (Dibasic magnesium phosphate)	Mg (2)	7.8	40.79	
			Magnesium tetrahydrogen diorthophosphate (Monobasic magnesium phosphate)	Mg (1)	3.7	52.00	
			Aluminum orthophosphate	Al (3)	8.3	57.24	

For classification of phosphates, we depend on "Encyclopedia of. Chem. Tech." 10 p. 404 (1953), The Interscience Encyclopedia, INC., N. Y.

was measured and converted to its logarithmic value. The logarithmic value was named the index of inhibition time. The relationship between the index of inhibition time and the corrosion potential was examined.

2. Experimental

2.1 Sample

The composition and preparation of viscoplastic substance used in this experiment were the same as of those used in the previous investigations.²⁾ The phosphates used were of commercial grade and their purities were examined by X-ray diffraction. The classification of phosphates is shown in Table 1.

2.2 Corrosion Potential

The measurement of the corrosion potential in viscoplastic substances, the potential *vs.* time curve obtained, and the apparatus used, have already been previously²⁾ described.

2.3 Index of Inhibition Time

30 g of the viscoplastic substance were filled into an aluminum tube, of 99.8% purity and 4019.2 mm² surface area, prepared by cold impact extrusion. The tube was placed in the thermostat at 50°C. The time (in hours) needed for the expansion of tube was measured and converted to its logarithmic value, which the authors named "the index of inhibition time".

2.4 Measurement of Viscoplastic Substance by X-ray Diffraction Method

The sample was prepared for analysis by filling the convex surface (20 × 16 × 0.5 mm) of a glass holder with it. The X-ray diffractometer used was of "Geiger-flex GF-3 type" of Rigaku-Denki Co., Ltd. and the X-ray analyses of phosphates and aluminum were made following the Hanawalt method.³⁾

3. Results and Discussion

3.1 Corrosion Potential of Sample to which Various Phosphate were Added.

The corrosion potential of samples when phosphates, equivalent to 1% P₂O₅, were added to the medium, is shown in Fig. 1.

Fig. 1 Influence of phosphates on corrosion potentials.

The result obtained showed that the corrosion potential upon addition of alkali earth metal monobasic orthophosphates and alkali earth metal dibasic orthophosphates such as magnesium tetrahydrogen diorthophosphate, magnesium hydrogen orthophosphate, calcium tetrahydrogen diorthophosphate and calcium hydrogen orthophosphate is shifted toward the noble value side and the same happened upon addition of sodium hexametaphosphate. But the corrosion potential upon addition of disodium hydrogen orthophosphate, trisodium orthophosphate, tricalcium diorthophosphate, sodium tripolyphosphate and sodium pyrophosphate shifted toward a value less noble than that of the blank. When sodium dihydrogen orthophosphate, trimagnesium diorthophosphate and aluminum orthophosphate were used, the corrosion potential was more noble than that of the blank but after some time, it was shifted toward a less noble value.

Table 2 Relationship Between Stationary Corrosion Potential and the Index of Inhibition Time

	Na(3)	Ca(3)	Na(P)	Na(T)	Na(2)	Blank	Al(3)
Index of inhibition time	0.48	1.08	1.08	1.08	1.38	1.38	1.68
Stationary corrosion potential (V)	-1.38	-1.34	-1.28	-1.24	-1.17	-1.17	-1.06
pH of the viscoplastic substance	11.5	11.8	10.5	9.8	9.5	9.0	8.7

	Na(1)	Mg(3)	Ca(2)	Ca(1)	Mg(2)	Na(H)	Mg(1)
Index of inhibition time	1.98	3.16	>3.46	>3.46	>3.46	>3.46	>3.46
Stationary corrosion potential (V)	-0.87	-0.85	-0.59	-0.55	-0.51	-0.52	-0.48
pH of the viscoplastic substance	6.8	9.3	7.9	7.5	7.9	7.4	6.6

3.2 Index of Inhibition Time of Samples to which Various Phosphates were Added

As shown Table 2 and Fig. 2, the results obtained from the index of inhibition time measurements were similar to those obtained by the measurements of corrosion potential. Accordingly, the measurement of the index of inhibition time was adopted as an effective means in the study of corrosion in viscoplastic substance. As the corrosion proceeded, the relationship among the pH of the viscoplastic substance, the stationary corrosion potential and the index of inhibition time were found to correlate quite nicely, as shown in Fig. 2.

The stationary corrosion potential became less noble and the index of inhibition time decreased with the increasing pH of the viscoplastic substance.

Fig. 2 Relationship between index of inhibition time, stationary corrosion potential and the pH of the paste.

3.3 Relationship Between the Concentration of Phosphates and Corrosion Potential

The relationship between the concentration of sodium hexametaphosphate added and the corrosion potential is shown in Fig. 3. When the concentration was

Fig. 3 Relationship between the concentration of sodium hexametaphosphate and the corrosion potential.

below 0.1 wt%, the corrosion potential was shifted toward a less noble value in the lapse of time, and no inhibitive action was found to exist. When the concentration was above 0.2 wt%, the corrosion potential was shifted toward nobler values and the stationary corrosion potentials were almost constant. The results obtain-

ed showed that the addition of 0.2 wt% (0.13 wt% P_2O_5) of sodium hexametaphosphate was enough to inhibit the corrosion of aluminum.

The relationship between the concentration of magnesium hydrogen orthophosphate added and the corrosion potential is shown in Fig. 4. When the addition concentration was below 0.1 wt%, the corrosion potential was shifted toward a less noble value. When the concentration was above 0.4 wt%, the potential was shifted toward noble. The above mentioned result shown that the addition 0.4 wt% (0.16 wt% P_2O_5) of magnesium hydrogen orthophosphate was enough to inhibit corrosion.

Fig. 4 Relationship between the concentration of magnesium hydrogen orthophosphate and the corrosion potential.

3.4 Relationship Between the Thermal Treatment of Sodium Hexametaphosphate and the Corrosion Potential

Sodium hexametaphosphate had an amorphous structure. It was converted into crystalline sodium metaphosphate by a thermal treatment, as shown in Fig. 5. The results given in Fig. 5. show that sodium hexametaphosphate is not converted to crystalline structure by thermal treatment of 200°C, but a part of the structure is

Cu K α 32KV-20mA F.C.S. 400cps Time const. 2sec.

Fig. 5 Structural change of sodium hexametaphosphate after thermal treatment.

converted to crystalline at 300°C, and when temperature reaches 400°C, all of the material is converted to crystalline sodium metaphosphate. The change of the stationary corrosion potential of the sample as a function of the thermal treatment, is shown in Fig. 6. When

Fig. 6 Relationship between thermal treatment of sodium hexametaphosphate and the stationary corrosion potential.

amorphous sodium hexametaphosphate was converted to the crystalline form, the stationary corrosion potential of the sample was a little shifted toward a less noble value. When a soluble phosphate such as sodium hexametaphosphate was converted from the polymeric amorphous structure to the crystalline monomer, its inhibition effect decreased. The fact above-mentioned is similar to that observed with soluble silicate compounds.²⁾ The inhibitive action increased with an increasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. Accordingly, colloidal and highly polymerized substances are considered to have a strong inhibitive effect on the corrosion of metals by viscoplastic substances.

3.5 Behavior of Phosphates in Viscoplastic Substance

The investigation of the behavior of several phosphates in the viscoplastic medium is very important for the understanding of the mechanism of inhibition. The results of the investigations of the behavior of phosphates, performed by the X-ray diffraction method are shown in Fig. 7 and Table 3. As shown in Fig. 7, the diffraction pattern of calcium tetrahydrogen diorthophosphate was not observed, but those of calcium hydrogen orthophosphate and tricalcium diorthophosphate or apatite were found in the medium, when the soluble calcium tetrahydrogen diorthophosphate was used. The diffraction patterns of calcium hydrogen orthophosphate and tricalcium diorthophosphate show clearly, proving that these are not soluble in the medium, while the contrary is true in the case of calcium tetrahydrogen diorthophosphate.

Sodium dihydrogen orthophosphate, disodium hydrogen orthophosphate and trisodium orthophosphate were converted to hardly soluble phosphates such as calcium hydrogen orthophosphate or tricalcium di-

orthophosphate. Due to the free alkali released in the medium in the case of sodium orthophosphate, the pH of viscoplastic substance was shifted towards the basic side, and the stationary corrosion potential shifted to a less noble value with the increasing pH of the sample.

Fig. 7 Structure of calcium phosphates in the viscoplastic substance.

In the case of alkali earth metal tetrahydrogen diorthophosphates, they were converted to alkali earth metal hydrogen orthophosphates and tri alkali earth metal diorthophosphates in the medium, but the corrosion potential and the index of inhibition time were different from those of alkali metal dihydrogen orthophosphates.

The sample to which alkali metal dihydrogen orthophosphate was added, was more corrosive than that to which alkali

Table 3 The Behavior of Phosphates in the Viscoplastic Substance

Classification	Phosphate	pH of paste	Structure	Structure in paste
Ortho phosphate	Na(3)	11.5	$\text{Na}_3\text{PO}_4 \cdot 1.2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	Na(2)	9.5	$\text{Na}_2\text{HPO}_4 \cdot 1.2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
	Na(1)	6.8	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
	Ca(3)	11.8	$\text{Ca}_3(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
	Ca(2)	8.2	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	Ca(1)	7.5	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
	Mg(3)	9.3	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
	Mg(2)	7.9	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	Mg(1)	6.8	$\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	Al(3)	8.7	Al PO_4	Al PO_4
Condensed phosphate	Na(H)	7.4	$(\text{NaPO}_3)_n$	Unknown pattern
	Na(T)	9.8	$\text{Na}_5\text{P}_3\text{O}_{10}$	Unknown pattern
	Na(P)	10.5	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	Unknown pattern

earth metal tetrahydrogen diorthophosphate was added. Thus we concluded that alkali metal salts and alkaline earth metal salts influenced the pH of the medium and the corrosive behavior of isolated hydroxide and carbonates in a different way.

Phosphates of magnesium had higher inhibitive effect than phosphates of calcium and the value of the stationary corrosion potential of the sample to which trimagnesium diorthophosphate was added was more noble than that of the blank. Accordingly, the sample to which phosphate of magnesium has been added, is considered to possess inhibitive properties.

The above mentioned results indicate that the following requirement was necessary for orthophosphates in the case of the corrosion of aluminum in viscoplastic substance. It should slightly dissolve and react with the metal. It should not release much free alkali and the pH of viscoplastic substance should not be largely shifted towards the basic side.

3.6 Investigation of the Inhibitive Effect by the X-ray Diffraction Method, Using Metal Powder

Studies on the corrosion behavior under slightly corrosive conditions were enhanced by the use of metal powder of very large surface area. Accordingly, aluminum powder of 99.7% purity was mixed into the viscoplastic substance and its corrosion behavior was measured by the X-ray diffraction method.

Condition of the X-ray diffraction tests were as follows: CuK α , 32kV-20mA, Scale factor 8, Time const. 2 sec.

The relationship between the concentration of aluminum powder and the intensity of the aluminum diffraction pattern is shown in Fig. 8. An amount of sodium hexameta-phosphate equivalent to 1% P₂O₅ was added to the medium in order to cause inhibition of the corrosion of aluminum in the case illustrated in Fig. 8. As shown in Fig. 8, a linear relationship between the intensity

Cu K α , 32KV-20mA, F.C.S. 400cps,
Time const. 2sec.

Fig. 8 Relationship between the concentration of Al powder and the X-ray diffraction intensity.

of the diffraction pattern of aluminum at $d=2.33 \text{ \AA}$ and the concentration of aluminum powder. Accordingly, the inhibitive effect of several phosphates was investigated using the calibration curve of the strongest diffraction pattern of aluminum at $d=2.33 \text{ \AA}$.

Fig. 9 deals with a sample to which trisodium phosphate has been added and illustrates the change in the intensity of the aluminum diffraction pattern, with time. The corrosion of this sample extremely increased and about half of aluminum powder was penetrated for 5 hours from the start.

The sample to which several phosphates,

Tri sodium orthophosphate P_2O_5 1%, Al powder 5%

Fig. 9 Corrosion behavior of aluminum after the addition of trisodium orthophosphate.

equivalent to 1% P_2O_5 were added, were placed in a thermostat at 30°C for 3 days, and the aluminum metal content of the samples was investigated by X-ray diffraction. Table 4 shows that the results of the measurement of X-ray diffraction were similar to those of the stationary corrosion potential and of the index of inhibition time. Accordingly, it was concluded that the measurement of X-ray diffraction and the use of metal powder in a viscoplastic substance provide a very simple and effective way for conducting test of the corrosive power viscoplastic substance.

Table 4 Results of the X-ray Diffraction Measurement Using of Al Powder (30°C 3 days)
Inhibition Percentage % = (Final quantity of Al powder/Initial quantity of Al powder) $\times$ 100

	Na(H)	Ca(2)	Na(1)	Blank	Na(2)	Na(T)	Na(P)	Na(3)
Inhibition percentage (%)	100	100	100	74	40	46	34	20
Stationary corrosion potential (V)	-0.52	-0.59	-0.87	-1.17	-1.17	-1.24	-1.28	-1.38
Index of inhibition time	>3.46	>3.46	1.98	1.38	1.38	1.08	1.08	0.48

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